

AMRL-TR-71-71

ADØ733709
citation



**TANDEM THERMOGRAVIMETRIC ANALYZER —
TIME-OF-FLIGHT MASS SPECTROMETER SYSTEM
DESIGNED FOR TOXICOLOGICAL EVALUATION
OF NONMETALLIC MATERIALS**

GERD A. KLEINEBERG, PhD.

DAVID L. GEIGER

OCTOBER 1971

20060707086

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AEROSPACE MEDICAL RESEARCH LABORATORY
AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Aerospace Medical Research Laboratory Aerospace Medical Div, Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE TANDEM THERMOGRAVIMETRIC ANALYZER — TIME-OF-FLIGHT MASS SPECTROMETER SYSTEM DESIGNED FOR TOXICOLOGICAL EVALUATION OF NONMETALLIC MATERIALS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report January 1970 - August 1971			
5. AUTHOR(S) (First name, middle initial, last name) Gerd A. Kleineberg, Ph.D. David L. Geiger			
6. REPORT DATE October 1971		7a. TOTAL NO. OF PAGES 14	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AMRL-TR-71-71	
b. PROJECT NO. 6302			
c. Task 630203		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d. Unit 007			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Aerospace Medical Research Laboratory Aerospace Medical Div, Air Force Systems Command, Wright-Patterson AFB, OH 45433	
13. ABSTRACT <p>An automatic electrobalance has been coupled in series with a mass spectrometer. The balance is part of a thermogravimetric analysis (TGA) system which also consists of a furnace with temperature programming capability and a strip chart recorder. A heated stainless steel capillary tube leading from close proximity of the sample inside the TGA instrumentation to the ion source of the mass spectrometer functions as the interface of the two system components. The Time-of-Flight mass spectrometer with its inherent high speed scanning capability has been modified to include a variable output integrator. This combination enables the toxicologist to relate conventional thermogravimetric analysis information to the unequivocal identification of potentially toxic thermal decomposition products. Newly developed fire retardant materials for use in interiors of passenger and cargo aircraft are analyzed to provide information on which to evaluate their toxicity potential under conditions of normal use and catastrophic situations such as fire.</p> <p>Key Words: Toxicology Space Cabin Toxicity Fire Retardant Materials Thermogravimetric Analysis System</p>			

FOREWORD

This report was prepared by members of the Chemical Hazards Branch, Toxic Hazards Division, Aerospace Medical Research Laboratory. This work was performed in support of Project 6302, "Toxic Hazards of Propellants and Materials," Task 630203, "Identification of Toxic Materials." The report covers work conducted from January 1970 to August 1971.

The authors wish to express their sincere gratitude and deep appreciation to Mr. Roland S. Gohlke, Eastman Kodak Company, Rochester, N.Y., for all of his technical comments, suggestions and criticisms.

This technical report has been reviewed and is approved.

CLINTON L. HOLT, Colonel, USAF, MC
Commander
Aerospace Medical Research Laboratory

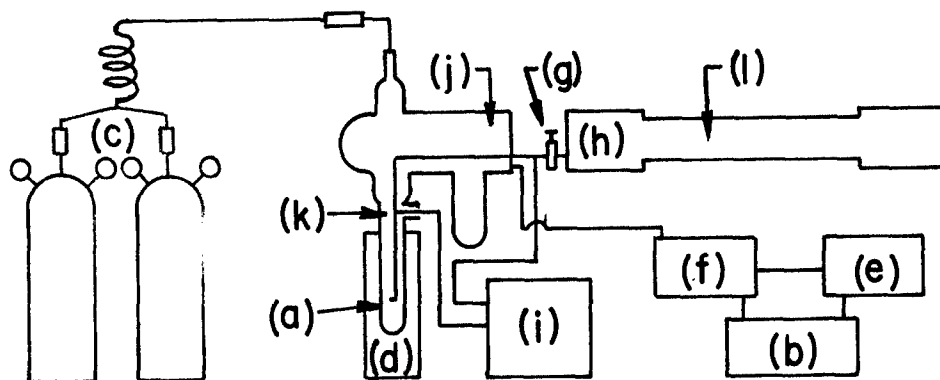
INTRODUCTION

High temperature resistant polymers and other nonmetallic materials that are relatively nonflammable are constantly being developed for use in areas containing potential ignition sources. The activity of the United States Air Force in this field is specifically directed to minimizing fire hazards in enclosed habitable spaces such as the interiors of passenger and cargo aircraft. Since the improved materials are often synthesized from toxic chemicals and are also subject to thermal degradation by virtue of their specific application, the nature of gas-off and degradation products and their toxicity becomes of paramount concern. These factors are particularly important when materials are employed in areas not exposed to view or ready detection, whereby thermal degradation may occur without visible recognition.

About 300 different materials were investigated for the National Aeronautics and Space Administration (NASA) in a 5-year program performed by the Aerospace Medical Research Laboratory (1-5). The instrumental approach chosen for the chemical analytical determinations prior to the toxicological evaluation was concurrent gas chromatographic, mass spectrometric, and infrared spectrophotometric analyses. These investigations for the identification and quantitation of thermal degradation and gas-off products were very elaborate and time consuming. For the screening of a large number of materials, a more simple approach with preferably the same accuracy was highly desirable. Thermogravimetry and mass spectrometry performed simultaneously on the same sample seemed to be a promising alternative. Coupling of thermal analysis instrumentation to mass spectrometers of various types has been reported earlier (6-10). The techniques described in these reports suffer from several deficiencies with respect to obtaining valuable information for toxicological evaluation. For instance, a) the sample is analyzed under a reduced pressure environment; b) the evolved components from the degrading specimen are trapped and subsequently transferred to the analyzing equipment; and c) a diffusion controlled time lapse between evolution and detection occurs. A more ideal approach is an analytical procedure that eliminates possible back contamination of consecutively evolving components and provides an immediate detector response. Consequently, a tandem thermogravimetric analyzer - Time-of-Flight mass spectrometer system was built for the identification of thermal decomposition and gas-off products to obtain the analytical information needed for subsequent toxicological evaluation of candidate high temperature resistant or nonflammable materials.

INSTRUMENTATION

The thermogravimetric analyzer - mass spectrometer system represents a multi-component arrangement which is outlined in the block diagram depicted in Figure 1.



- | | |
|-----------------------|--------------------------------|
| (a)CAPILLARY | (g)VALVE |
| (b)RECORDER | (h)IONISATION SOURCE |
| (c)GAS MIXING SYSTEM | (i)DC POWER SUPPLY |
| (d)FURNACE | (j)CAHN RH ELECTRO-
BALANCE |
| (e)PROGRAMMER | (k)HANGDOWN TUBE |
| (f)BALANCE CONTROLLER | (l)MASS SPECTROMETER |

-Figure 1. Thermogravimetric Analyzer - Time-of-Flight Mass Spectrometer

The function of these components during the course of an analysis can be described as follows. A sample of appropriate size and shape taken from the material to be investigated is placed in a platinum stirrup pan measuring 9mm in diameter. The pan is freely suspended from a wire inside a quartz hangdown tube (k) of 23mm inner diameter on the sample loop of a conventional Cahn RH electrobalance (j). The sample is positioned in such a way as to be about 5mm underneath the tip of a stainless steel capillary which is bent slightly upward (a), and also at about the same distance (5mm) from the fused tip of a chromel-alumel thermocouple used to record the sample temperature on one channel of the dual pen strip chart recorder (b). From a gas mixing system (c), a gas composition selected for analysis is flowed through the balance bottle entering the hangdown tube simultaneously from the top and from the bottom and exiting through a sidearm. After complete purging, the clam

shell furnace (d), is brought into position so that the sample is located in its center. Two platinum thermocouples are placed inside the furnace adjacent to the hangdown tube at about the same location. One thermocouple serves as the control for the furnace and the second feeds its signal into the indicating pyrometer of the programmer (e) that activates a lower and upper limit control. The sample weight is then accurately determined by adjusting the weight trace on the second channel of the dual pen recorder to its desired position and by noting the line divisions on the chart and the mass dial indication of the balance controller (f). After selecting the desired temperature programming rate, mode of operation, the desired weight range for a full scale deflection of the weight trace, and the proper mV range for the signal recording from the sample thermocouple, the thermogravimetric analyzer is ready for the actual analysis.

Concurrent with the preparation of the balance the mass spectrometer (Bendix, Model 12 with extended flight tube) is readied for operation. After the cryogenic trap of the mass spectrometer vacuum system is charged with liquid nitrogen, the valve (g) of the capillary is opened to the ionization source of the spectrometer (b), thus completing the interfacing of the thermogravimetric analyzer and the mass spectrometer. The capillary employed is 900 mm in length and has an inner diameter of about 0.25 mm. In order to achieve the necessary pressure drop between the sample location and the ionizing region inside the electron bombardment source to maintain a tolerable total pressure for the operation of the mass spectrometer, the capillary had to be modified. According to the following equation

$$R = k \frac{l}{d^4} \quad (1)$$

where R represents the gas flow resistance and where l is the length, d the diameter, and k the characteristic proportionality constant for the restriction, an effective flow regulation can be achieved by varying either l or d, or both. Since the length of the capillary had to remain the same and because it was impractical to alter the diameter, the necessary flow restriction could only be obtained conveniently by adding a restricting orifice. It is imperative that this orifice is located as close as possible to the sample in order to avoid an undesirable time delay for the evolved decomposition products to reach the ion source of the mass spectrometer. Dimensional restrictions inside the hangdown tube prohibited the use of any suitable type of mechanical valve. For this reason the tip of the capillary was carefully crimped to form a restriction in the transfer line that yielded a total gas pressure inside the ion source of 2 to $3 \cdot 10^{-5}$ torr when the tip was at ambient pressure. This reduced pressure does not interfere with normal operation of the Time-of-Flight mass spectrometer.

The mean free path of the sample molecules entering the restricted orifice at the tip of the capillary is small compared to the diameter of the restriction. Under this condition viscous flow exists and no mass discrimination occurs. Experiments were performed with the capillary tip sealed inside a flask containing test compounds in the parts per million (ppm) range at ambient pressure. Upon opening the isolation valve (g) the mass spectrometer response to these compounds was instantaneous. Therefore, a virtually simultaneous analysis of weight loss and mass spectrometric identification can be performed. We demonstrated that sufficient sample enters the ion source through the capillary. Using the mass spectrometer parameters usually employed in our investigations (i.e. electron energy: 70V; ionizing current: $0.5 \cdot 10^{-6}$ amp; scan rate: 134 sec from amu 12 to 200; ion source temperature: 850°C) a concentration of 11.0 ppm methane (CH_4) yielded a total ion current, for m/e at 16, of 50×10^{-12} amp. This current is sufficient to drive the galvanometer trace off scale.

In order to prevent higher boiling material from condensing when sample is flowing through the capillary, the line is conductively heated employing the DC power supply (i).

A background mass spectrum is recorded before the analysis is started and this spectrum subtracted from the ones subsequently recorded to identify thermal degradation or gas-off products. After the heating of the sample is initiated and as soon as a weight change is indicated by the weight trace on the recorder a complete mass spectrum is recorded with the mass spectrometer. Mass range and scanning rate are selected for optimum conditions in each case. A subsequent scan can be performed as soon as the previous one is completed. Normally scanning rates of 5.5 sec to 134 sec for atomic mass units between 12 and 200 are used. A complete history of the evolved material from the sample at distinct points of weight loss and temperature is thus obtained. After these data have been evaluated and a potentially toxic material has been identified, the mass spectrometer can be used to monitor for this compound exclusively during a subsequent analysis made under otherwise identical conditions. In addition, a variety of environmental conditions for the sample can be achieved utilizing the gas mixing system, and by employing any of the different temperature profiles possible. Condition changes from those of normal use of the sample under investigation to a situation as it exists during a fire can be simulated. The data obtained with this instrument combination are much more detailed and complete than those obtained from sequential analyses employing various instrumental approaches. From the wealth of information that can be obtained with the thermogravimetric analyzer - Time-of-Flight mass spectrometer system a few examples are discussed in the following section.

MEASUREMENTS

A sample of Nomex, standard Air Force issue, used for flight suits, was analyzed for comparative investigations regarding the thermal degradation and toxicity with respect to more advanced materials of chemically similar nature. The Nomex cloth was subjected to a variety of environmental conditions. As an example, a thermogravimetric (TG) pattern of a specimen chosen for analysis under ambient air with a temperature increase of 10° per minute is shown in Figure 2. Under these conditions the aromatic polyamide has been completely disintegrated upon reaching a temperature of 560°C over a period of 54 minutes, leaving a residue of only 2%. The weight trace shows a decrease of 4% of the sample in the temperature range between 60° and 115°C . After this point the weight remains constant up to about 375°C where a moderately rapid weight loss sets in. A first maximum of decomposition occurs at about 440°C with 17% of the sample lost. The remainder of the material decomposes rapidly between 510° and 560°C , reaching a second maximum at about 525°C .

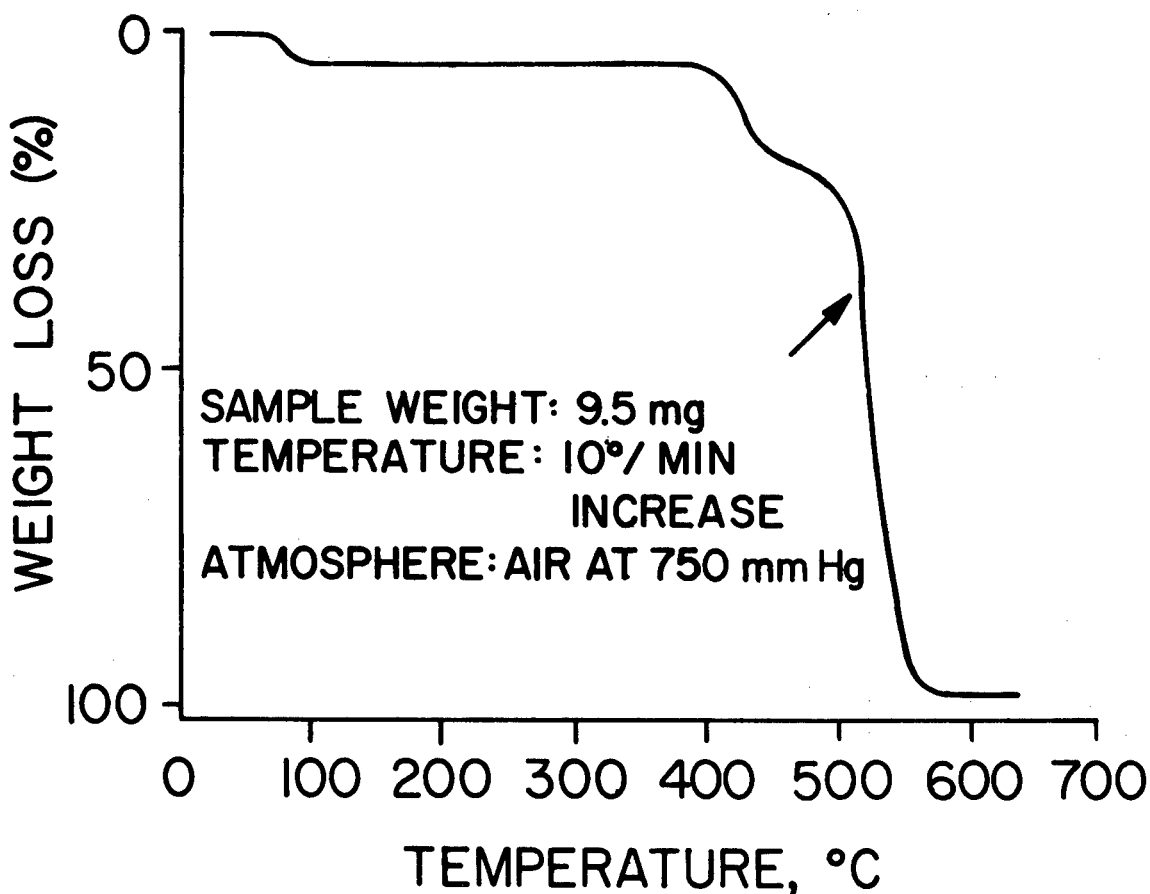


Figure 2. Weight-Change Pattern of a Nomex Sample

As soon as the weight trace on the strip chart recorder indicated a weight loss of the sample at 60°C, a mass spectrum was recorded. As the weight change continued up to 115°C a total of five spectra were recorded with a scanning rate of 60 sec each between the atomic mass units of 12 to 200. During the intermittent period of constant weight several mass spectra were obtained routinely. Starting at the point of further decomposition at 385°C, fifteen additional mass spectra were scanned over the same mass range at the rate of 60 sec each.

The interpretation of the first five mass spectra revealed that the weight loss of the Nomex sample recorded for the interval of 60° to 115°C was due exclusively to the loss of water. No appreciable amounts of any other evolved gases from the sample up to 405°C could be found. Above this temperature the formation of carbon dioxide increased rapidly concomitant with an increase in water vapor concentration. The variable total output integrator of the mass spectrometer was set to monitor the total ion output of all singly charged particles of 44 atomic mass units and above. At the point of maximum output indication a mass spectrum was recorded, as marked by the arrow in Figure 2. Figure 3 shows this spectrum subtracted from the background scan that was recorded prior to initiation of the temperature program. The spectrum with peaks showing at 44, 18, 17, and 12 atomic mass units (amu) suggests that carbon dioxide (CO_2 : amu 44, C amu 12), water (H_2O : amu 18, OH: amu 17), and possibly N_2O with the same amu of 44 as CO_2 are the sole degradation products of the Nomex sample treated under the reported conditions. Additional analyses performed under varying conditions with approximately the same amount of oxygen available confirmed these findings.

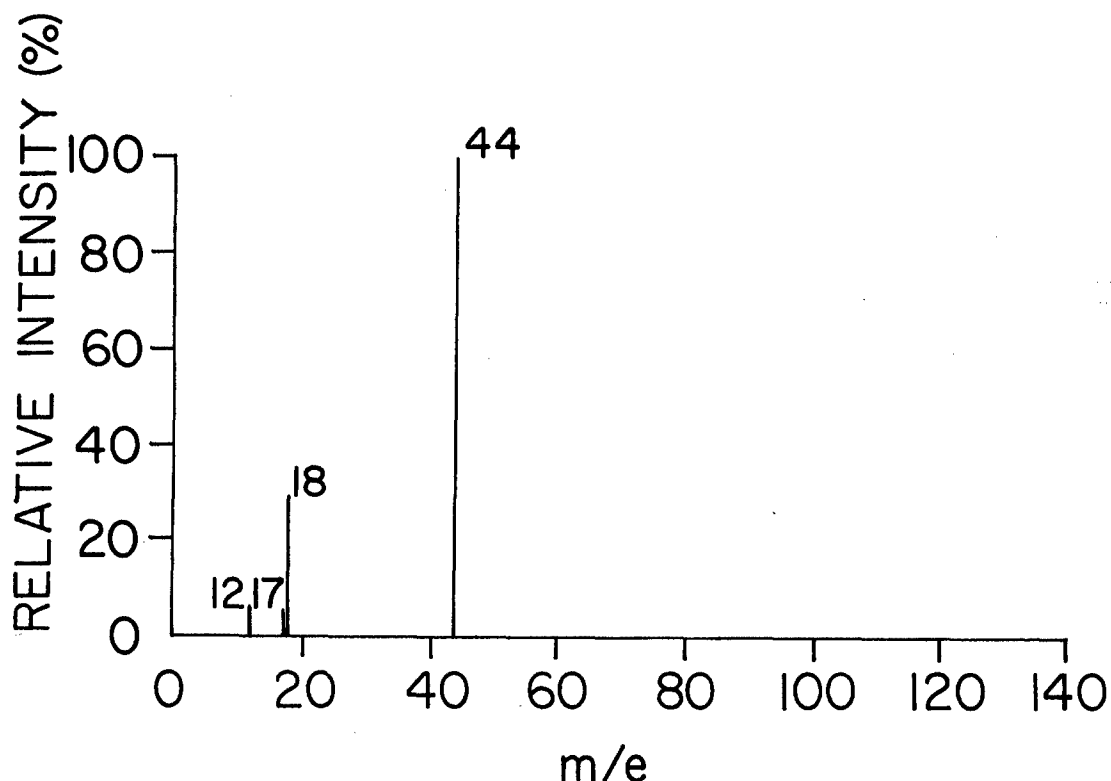


Figure 3. Mass Spectrum of Combustion Products of a Nomex Sample

In a similar fashion samples of polybenzimidazole (PBI) fabric (Celanese fiber) were analyzed. Figure 4 shows the thermogravimetric pattern of a PBI sample investigated under an atmosphere where argon was substituted for nitrogen to reserve the space in the mass spectra at atomic mass unit 28 for the detection of carbon monoxide (CO) that could possibly be formed during degradation of the sample. One of the four analog scanners of the mass spectrometer was connected to a strip chart recorder to monitor the total ion current at the atomic mass unit 30 during the entire analysis. The broken line in Figure 4 represents the measured output. Two discrete steps of weight loss are apparent from the solid line which represents the weight trace. During the thermal analysis, mass spectra were recorded at the same rate as with Nomex. The first step of weight loss was exclusively due to the evaporation of water. At the time of the most rapid decomposition during the second phase of weight loss as indicated by the output integrator of the mass spectrometer and marked by the arrow in Figure 4, the mass spectrum as shown in Figure 5 was recorded.

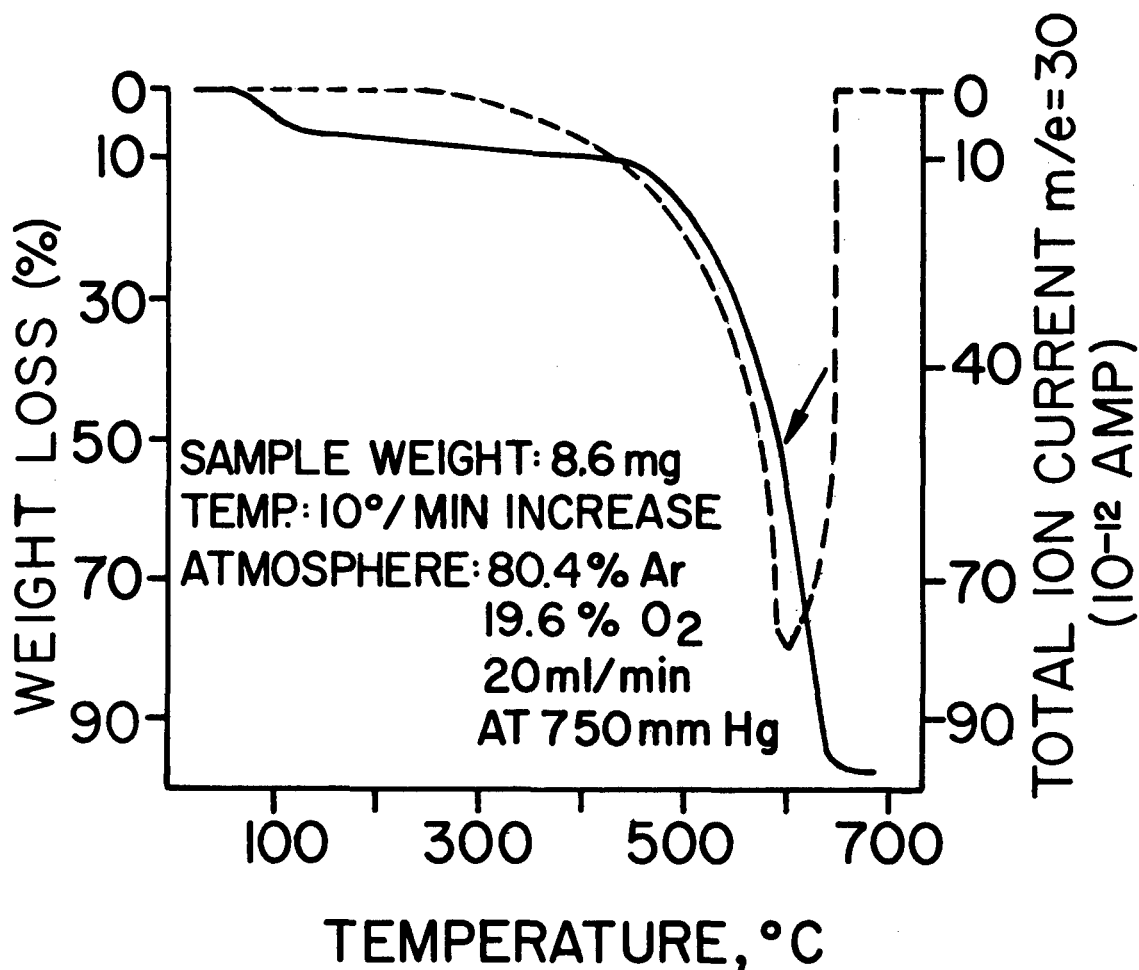


Figure 4. Weight-Change Pattern of a PBI Sample

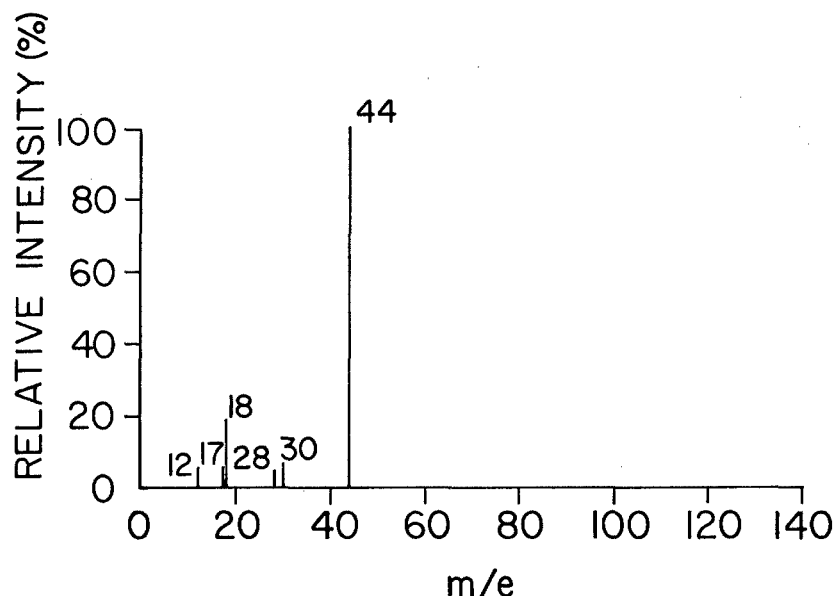


Figure 5. Mass Spectrum of Combustion Products of a PBI Sample

The mass spectrum of the evolved gases from the PBI sample obtained at this point under the reported conditions is representative for all additional scans made during the second phase of decomposition. The peak appearing at 30 amu indicates the presence of nitrous oxide (NO). This information is most valuable to the toxicologist.

The data obtained from these two fabrics were straightforward and did not give rise to any particular concern with respect to the usage of these two materials. An example of a more complex situation is the result of an investigation employing carboxynitroso rubber. Figure 6 is a typical weight change pattern for this polymeric material, and it is also representative for several samples of various origin that were investigated.

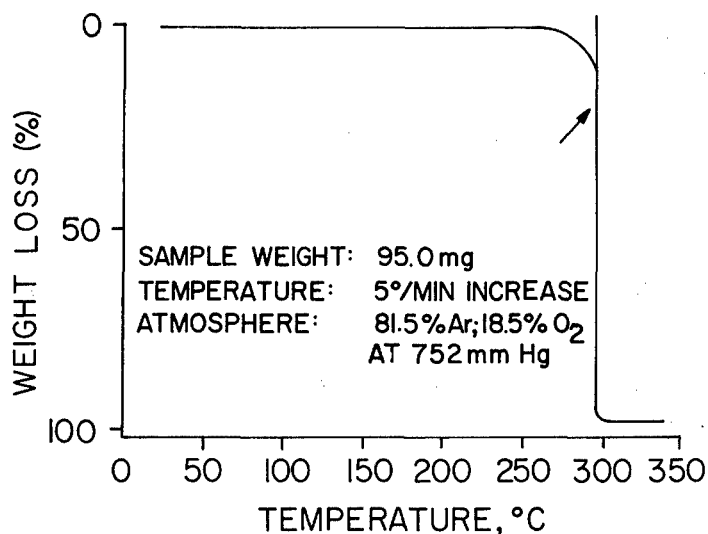


Figure 6. Weight-Change Pattern of a CNR Sample

Up to about 250°C the rubber does not undergo appreciable weight change. Above this temperature a moderate sample loss occurs and at further temperature increase an abrupt, complete decomposition takes place. The spike in Figure 6 at 292°C results from a sudden downward force applied to the sample pan by the evolving gases produced during the extremely rapid decomposition at this temperature. Exactly at this point a mass spectrum for the evolved gas analysis was recorded. Figure 7 shows this spectrum subtracted from the background scan that was recorded at room temperature.

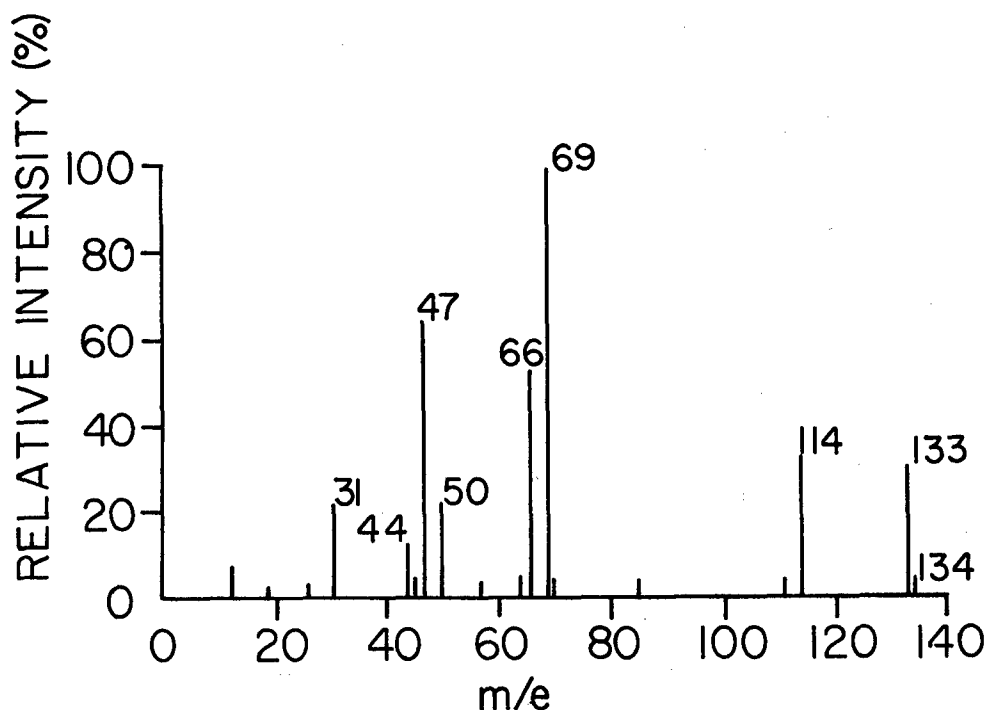
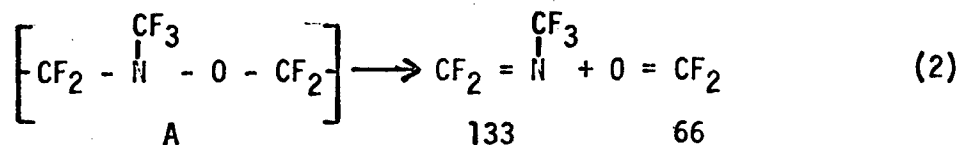


Figure 7. Mass Spectrum of Decomposition Products of a CNR Sample

The correlation of the mass peaks suggests a breakdown mechanism and clearly identifies the decomposition products formed. A primary reaction for the degradation that yields equimolar amounts of carbonylfluoride and perfluoro - N - methylmethylenimine can be postulated by the presence of peaks at 66 and 133 amu. The cleavage of the polymer building block (A) occurs in this case between the oxygen and nitrogen atoms.



The peaks at 133 amu and 66 amu represent the molecular ion peaks of the respective degradation compounds. The imine fragment ions formed in the ion source account for the additional peaks that are tabulated in Table I.

Table 1

FRAGMENT IONS DERIVED FROM PERFLUORO - N - METHYLMETHYLENIMINE

<u>amu</u>	<u>fragment ion</u>
69	CF ₃
114	CF ₂ NCF ₂
31	CF ₂ ⁺
50	CF ₂
45	FCN
26	CN
57	FCCN
64	F ₂ CN
12	C
19	F

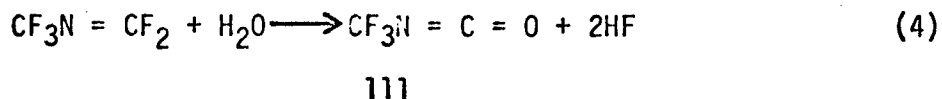
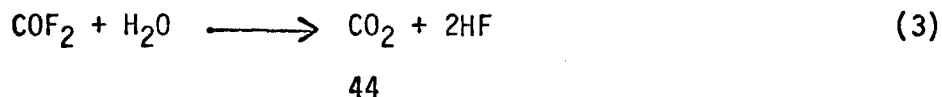
The fragment ions formed from carbonylfluoride gave rise to the peaks listed in Table 2.

Table 2

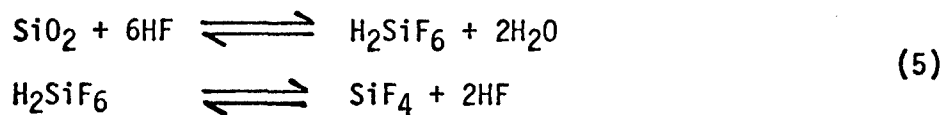
FRAGMENT IONS DERIVED FROM CARBONYLFLUORIDE

<u>amu</u>	<u>fragment ion</u>
47	COF
50	CF ₂
31	CF ₂ ⁺
19	F

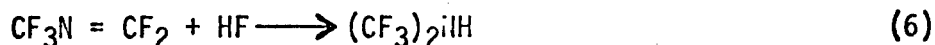
The primary reaction products undergo secondary reactions with water vapor undoubtedly present as shown in the following equations:



The formation of carbon dioxide and the isocyanate derivative accounts for the peaks found at the atomic mass units of 44 and 111. The hydrofluoric acid formed in these reactions will attack the glass of the TG - system and form the following reaction sequence:



The silicon tetrafluoride formed does not show a molecular ion peak in the mass spectrum; rather, its presence is indicated by the fragment ion peak at 85 amu for SiF_3 . Hydrofluoric acid will also react with the imine as indicated below:



Again, the perfluorodimethylamine does not exhibit a molecular ion peak because perfluoro compounds very readily split off a fluorine atom giving rise in this case to the peak at 134 amu for the fragment $\text{CF}_3\text{-NH-CF}_2$.

All mass peaks in the spectrum of Figure 7 have been accounted for and one can summarize that the compounds listed in Table 3 are present in the evolved gas from decomposing carboxynitroso rubber.

Table 3

DECOMPOSITION PRODUCTS FROM CNR

Carbonyl fluoride	COF_2
Perfluoro-N-methylmethlenimine	$\text{CF}_2=\text{N-CF}_3$
Trifluoromethylisocyanate	$\text{CF}_3\text{-N=C=O}$
Carbon dioxide	CO_2
Hydrofluoric acid	HF
Silicon tetrafluoride	SiF_4
Perfluorodimethylamine	$(\text{CF}_3)_2\text{NH}$

This list of compounds was reported to the toxicologist.

DISCUSSION

A tandem thermogravimetric analyzer- Time-of-Flight mass spectrometer system was built to identify thermal decomposition and gas-off products from nonmetallic materials. The analyzed compounds are newly developed high temperature resistant and nonflammable polymers that are candidates for use in enclosed habitable spaces of passenger and cargo aircraft. Using the instrumentation described a multitude of environmental parameters can be achieved and a variety of conditions can thus be applied for the samples under investigation. Normal usage, exposure to excessive heat, or a situation as it may exist during a fire, for example, can be simulated. The data that can be obtained encompass static and dynamic thermogravimetric determinations with simultaneous evolved gas identification under the same conditions. Trapping, enriching and transferring of sample is avoided to achieve instantaneous identification of primary reaction products formed. Selected components of evolved gases can be monitored exclusively as well as analysis of a composite atmosphere performed.

Chemical analytical data indicative of material behavior under a variety of conditions that are essential for a complete toxicological evaluation of candidate materials can thus be conveniently obtained in short periods of time. In addition, quantitative determination can be achieved through correlation of the mass spectrometric and the thermogravimetric data.

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